



Thermodynamic constraints on the formation of condensed carbon from serpentinization fluids

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Abstract

Recent studies have identified carbonaceous material in serpentinite bodies, but whether these deposits have a biologic or abiotic origin remains uncertain. In this work, thermodynamic calculations were performed to examine the potential for abiotic condensed carbonaceous material to be produced from serpentinization-derived fluids under hydrothermal conditions. Calculation of reaction pathways during serpentinization of olivine showed that fluid compositions should equilibrate with condensed carbonaceous material, which controls the H₂ and CO₂ activities. Fluids from laboratory serpentinization experiments and from the Lost City and the Rainbow hydrothermal field are shown to be consistent with this model. The predictions indicate that carbonaceous material should be the dominant carbon product of CO₂ reduction in these hydrothermal settings, which would have significant implications for a number of processes, including the deep Earth carbon cycle by creating a pool of relatively immobile reduced carbon, the extent of H₂ production in ultrabasic environments, and mechanisms leading to abiotic reduced carbon compounds.

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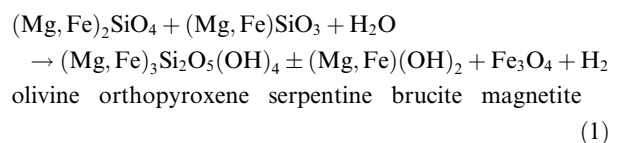
Keywords: Serpentinization; Carbon; Organic compounds; Abiotic; Hydrogen; Thermodynamic modeling

1. INTRODUCTION

It is widely recognized that the serpentinization of ultramafic rocks creates strongly reducing conditions that are favorable for abiotic reduction of inorganic carbon. Indeed, there is mounting evidence that fluids discharged from actively serpentinizing systems contain methane, formate and other simple organic compounds formed by abiotic carbon reduction within these systems (Charlou et al., 2002, 2010; Proskurowski et al., 2008; Lang et al., 2010; Etiope et al., 2013a,b; Etiope and Sherwood Lollar, 2013;

McDermott et al., 2015). In addition, a number of laboratory studies have demonstrated that methane and other small organic compounds can be generated from reduction of inorganic carbon at conditions simulating those of hydrothermal serpentinization fluids (Berndt et al., 1996; Horita and Berndt, 1999; McCollom and Seewald, 2001, 2003; Foustoukos and Seyfried, 2004; Seewald et al., 2006; Fu et al., 2007).

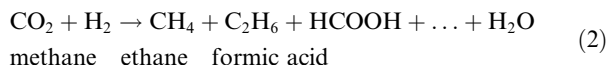
In general terms, the serpentinization of ultramafic rocks can be represented by the reaction:



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The generation of H₂ during this process results from oxidation of ferrous iron (Fe^{II}) released by the primary minerals through reaction with H₂O, producing ferric iron (Fe^{III}) that precipitates in magnetite or serpentine. The formation of methane and other organic compounds is generally thought to proceed from reduction of inorganic carbon by the H₂ generated by Reaction. (1), which can be expressed in general as:



While the evidence for abiotic generation of small organic compounds during serpentinization has gotten stronger over the last couple of decades, it has remained uncertain whether carbon reduction extends to more complex compounds. Holm and Charlou (2001) observed long-chain hydrocarbons (C₁₆–C₂₉) in extracts of hydrothermal fluids from the ultramafic-hosted Rainbow system on the Mid-Atlantic Ridge (MAR) which they inferred were derived from abiotic reduction of inorganic carbon by Fischer–Tropsch-type (FTT) processes. However, subsequent studies have not found any definitive evidence for long-chain hydrocarbons or other high-molecular-weight organic compounds with an abiotic origin at Rainbow or at other ultramafic-hosted sites on the MAR (Konn et al., 2009, 2012; McCollom et al., 2015). Delacour et al. (2008) identified a number of long-chain linear alkanes resembling those produced by FTT reactions in serpentinized rocks recovered near the Lost City hydrothermal field. However, the presence of biomarker compounds such as pristane and phytane indicated that there was a substantial contribution of biologically derived organic matter to the rocks, making evaluations of a possible abiotic source for the alkanes equivocal. In samples of deep altered oceanic crust, Shilobreeva et al. (2011) measured bulk carbon with a heavy isotopic composition that they explained as a mixture between carbonate and organic compounds produced from the abiotic reduction of magmatic CO₂. Recent studies by Ménez et al. (2012) and Pasini et al. (2013) identified macromolecular carbon deposits in serpentinites recovered from the seafloor, which were interpreted to be ultimately derived from biological organisms. Over the years, several studies reported the occurrence of graphite associated with serpentinites (e.g., Rao, 1964; Chidester et al., 1978; Pasteris, 1981, 1988; Luque et al., 1992, Luque del Villar et al., 1998; Miura et al., 2011; Galvez et al., 2013; Kawamoto et al., 2013). Although it has been suggested that these graphite deposits precipitated from reduction of CO₂ transported into the rocks by hydrothermal fluids, it remains undetermined how they actually formed.

A number of laboratory experimental studies have been performed to examine inorganic carbon reduction during serpentinization. However, these studies have predominantly focused on formation of CH₄ and light hydrocarbons (e.g., Berndt et al., 1996; Horita and Berndt, 1999; McCollom and Seewald, 2001, 2003; Foustoukos and Seyfried, 2004; Fu et al., 2007). In some of these studies, mass balance calculations indicate decreases in the amounts of dissolved inorganic carbon and of H₂ that cannot be

completely accounted for by production of methane and other small organic molecules, suggesting the possibility that more complex reduced carbon compounds had formed during the experiments. For example, Fu et al. (2007) observed formation of dissolved CO and C₁–C₃ hydrocarbons during reaction of magnetite with CO₂- and H₂-bearing aqueous fluids at 400 °C and 50 MPa. Mass balance calculations, however, indicated that ~14% of the inorganic carbon that had been included at the start of the experiments could not be accounted for by the observed products. Those authors suggested that more complex organic compounds had formed, such as longer-chain hydrocarbons. Similarly, in a recently completed series of hydrothermal serpentinization experiments with olivine as the reactant by McCollom et al. (2016), the amounts of H₂ produced during the experiments were up to 20% less than the amounts that should have been generated based on the Fe^{III} present in the reaction products. Since only trace amounts of methane and other dissolved organic compounds were observed, these results suggest that some other forms of reduced carbon may be required to account for the “missing” H₂.

These findings prompted us to investigate the potential for production of insoluble abiotic carbonaceous material during serpentinization. Thermodynamic calculations were performed to explore the ability of carbonaceous material to form and to control the H₂ and CO₂ compositions of aqueous fluids as the serpentinization reaction proceeds. The compositions of experimental and natural fluids reported in the literature are interpreted in the context of these thermodynamic models. The results have implications for diverse geologic disciplines including global carbon cycling, metamorphic petrology, and subsurface microbiology.

2. METHODOLOGY

To place the composition of natural and experimental fluids in a thermodynamic context, equilibrium phase diagrams were constructed for the Fe–O–H–C system. Comparison between fluid compositions and mineral stability domains allows the solid phases expected to precipitate at equilibrium to be identified, and to interpret which phases, if any, might control the fluid composition. The stability domains of minerals involved in the serpentinization reaction were calculated at temperatures from 100 to 400 °C and pressures of 35 and 50 MPa using parameters generated with the SUPCRT92 package (Johnson et al., 1992), which incorporates thermodynamic data from Helgeson et al. (1978) for minerals, and Shock and Helgeson (1988) and Shock et al. (1989, 1997) for dissolved inorganic aqueous species.

Predictions of the compositional paths of the fluid and coexisting solids as serpentinization proceeds were calculated with the geochemical code CHES (van der Lee et al., 2002). The CHES software simulates reactions between minerals and fluids, and determines the compositions of minerals and coexisting fluids at thermodynamic equilibrium through minimization of the Gibbs energy of the overall system for a given temperature at steam

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